

JAPANESE

[JP,2003-020401,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the polyamide resin composition excellent in the mechanical strength, the toughness, the heat resistance, the abrasion resistance, and the processability which consist of polyamide and a stratified mineral, its Plastic solid, and its manufacturing method.

[0002]

[Description of the Prior Art]The resin composition which strengthened polyamide with inorganic fillers, such as fibers, such as glass fiber and carbon fiber, and calcium carbonate, is known widely. However, these reinforcement are lacking in compatibility with polyamide, and the mechanical strength and heat resistance of strengthening polyamide have the problem that the camber of mold goods becomes large, in the resin composition which the toughness of what is improved fell and was strengthened with the fiber. And in the resin composition strengthened with these inorganic fillers, there was a problem that neither a mechanical strength nor heat resistance improved unless it blends a filler so much.

[0003]The resin composition which consists of polyamide and argillite represented by montmorillonite as a trial which improves the fault of such strengthening polyamide is proposed. This method is a thing aiming at manufacturing the complex which carried out uniform dispersion minutely by making a polyamide chain invade between the layers of argillite, For example, the resin composition which consists of polyamide and montmorillonite, and its manufacturing method are indicated by JP,62-74957,A, JP,1-301750,A, JP,2-866628,A, and JP,3-7729,A.

[0004]When using montmorillonite for such the purpose, as indicated in each of above-mentioned gazettes, Before blending montmorillonite with the monomer which forms polyamide or polyamide, the processing for extending the interlaminar distance of montmorillonite is made by contacting this to swelling agents, such as amino acid. It is indicating having the performance the reinforced polyamide resin composition which consists of polyamide and specific fluoride mica excelled [performance] in JP,6-248176,A. However, also in which method of these, once manufacturing reinforced polyamide resin, the fabricating operation had to be carried out using another processing device, but since it was strengthening resin, the melting resin streak was bad and there were problems, like the yield in a fabricating operation is low, or becomes a high cost.

[0005]In order to solve these problems, it is possible to use an anionic polymerization method, and the method of producing strengthening polyamide by an anionic polymerization method using a silicate is indicated by JP,62-252425,A. However, in this invention, it aims at narrowing

molecular weight distribution, and the polyamide of the amount of polymers was not obtained, and abrasion resistance was not improved.

[0006]

[Problem(s) to be Solved by the Invention]This invention tends to solve the above-mentioned problem, does not have the camber of mold goods, and A mechanical strength, They are the yield aggravation at the time of shaping, and a thing made profitably like with an easy forming process without carrying out a cost hike about the reinforced polyamide resin composition which was excellent in abrasion resistance in the amount of polymers excellent in toughness, heat resistance, and dimensional stability, and a work.

[0007]

[Means for Solving the Problem]In order to solve such a technical problem, as a result of repeating research wholeheartedly, this invention persons adopted reaction injection molding which performs this within a metallic mold using an anionic polymerization method, found out that an aforementioned problem solved a stratified mineral by adding and polymerizing to a monomer at the time of a polymerization start, and reached this invention.

[0008]That is, the gist of this invention is as follows.

1. as stratified as polyamide 100 mass part -- consisting of mineral 0.01-100 mass part -- the amount of amino terminals -- a with 10 mol [t] /or less and a relative viscosity [of four or more] (96% sulfuric acid, concentration of 1 g/dl) polyamide resin composition.
2. Polyamide resin Plastic solid which is Plastic solid acquired by reaction injection molding which performs anionic polymerization of lactam within metallic mold, and adds and obtains stratified mineral to monomer at time of start of anionic polymerization.
3. Manufacturing method of polyamide resin Plastic solid adding stratified mineral to monomer at time of start of anionic polymerization, and polymerizing in reaction injection molding which performs anionic polymerization of lactam within metallic mold.

[0009]

[Embodiment of the Invention]The polyamide used by this invention is polyamide produced by carrying out ring breakage of the lactam. As lactam, epsilon caprolactam, alpha-pyrrolidone, alpha-piperidone, ** [mixture / of omega-ENANTO lactam, omega-KAPURIRO lactam, omega-PERARUGONO lactam, omega-decanolactam, omega-undecanone lactam, omega-RAURO lactam or such c-alkylation-omega-lactam, and two or more sorts of such lactam] can be used. Such copolymerization polyamide and mixed polyamide can also be used.

[0010]As a basic catalyst in the anionic polymerization of this invention, alkaline metals, such as organic metal catalysts, such as a Grignard compound and an organolithium compound, sodium, and potassium, sodium hydride, lithium hydride (the lactam salt of these is included), etc. are used preferably. As for especially the amount of the basic catalyst used, it is preferred to consider it as 0.2-5-mol % to lactam 0.05-10-mol%. If a rate of polymerization falls less than [0.05 mol %] and the quantity of a catalyst exceeds 10-mol % on the other hand, it will become difficult to go up a molecular weight.

[0011]As an initiator of anionic polymerization, N-acetylcaprolactam, AJIPO yl screw caprolactam, acyl lactam compounds (carboxylic acid halide.), such as tele phthloyl screw caprolactam the compound which reacts to lactam, such as a carboxylic anhydride, and gives acyl lactam -- containing. Triallyl isocyanurate, N-substitution ethyleneimine derivative, a 1.1'-carbonyl screw aziridine, An oxazoline derivative, 2-(N-phenylbenzimidoyl) acetanilide, Compounds, such as 2-(N-phenylbenzimidoyl) acetanilide, 2-N-MORIHORI no cyclohexene 1.3-dicarbo KISANIRIDO, etc. publicly known isocyanate, a carbodiimide, can be used. Especially an acyl lactam compound is used preferably. the amount of the initiator used receives lactam -- 0.01-10-mol % -- it is preferably appropriate to 0.02-2-mol consider it as % still more preferably 0.02-5-mol%. A rate of polymerization becomes it small that the quantity of an initiator is less than [0.01 mol %], and on the other hand, if the quantity of an initiator exceeds 10-mol %, a molecular weight will not go up enough. By using these initiators in the above-mentioned density range, the amino terminal concentration of polyamide resin becomes lower 10 mol /than t, and the effect of decomposition being controlled is revealed.

[0012]As for the moisture regain in an anionic polymerization system, it is preferred to make it low. Although 0.001-0.1-mol% of the range is preferred to a monomer amount, in order to avoid that an initiator and a catalyst are deactivated, it is preferred to consider it as 0.1 or less concentration of initiator concentration further. However, in order to make moisture regain into less than [0.001 mol %], it is required, and special desiccation serves as a high cost and is not preferred.

[0013]Although the method of using driers, such as distillation under reduced pressure, vacuum drying, a molecular sieve, and silica gel, the method of leading an inactive dry gas, etc. are mentioned as a water removal method, the method of leading an inactive dry gas is the simplest, and removal efficiency is also high. Especially if it is a dry gas which does not have an adverse effect on the anionic polymerization of lactam as an inactive dry gas, it will not be limited, but argon or nitrogen gas is usually used preferably.

[0014]as for polymerization temperature, it is preferred to consider it as the range of 100 - 200 °C -- the range of 120 - 180 °C is more preferred. Polymerization temperature. A polymerization does not advance promptly that it is less than 100 °C, but on the other hand, if it exceeds 200 °C, a side reaction will occur and the fusibility to a solvent will fall. An addition order to a basic catalyst and the lactam of an initiator may be arbitrary.

[0015]The amino terminal concentration of polyamide resin needs to be 10 mol/t or less. In exceeding t in 10 mol /, the evil of decomposition being promoted at the time of a heating process occurs.

[0016]The molecular weight of the mixed polyamide resin used for this invention needs to use 96 mass % concentrated sulfuric acid as a solvent, it is necessary to make into an index temperature of 25 °C, and relative viscosity measured on conditions with a concentration of 1 g/dl, and to be 4.0 or more, and 8.0 especially or more are 10.0 or more desirable still more preferably. Relative viscosity tends to be inferior to the mechanical physical property of mold goods in less than 4.0 thing.

[0017]As a stratified mineral used by this invention, although the sheet silicate of swelling nature, such as fluoride mica, montmorillonite, and a smectite, is mentioned, swelling fluoride mica and montmorillonite are especially preferred. These may extend interlaminar distance beforehand by making a swelling agent contact.

[0018]The swelling fluoride mica system mineral used for this invention has a structural formula generally shown with a following formula, and is obtained by scorification or the intercalation method.

$M_a(Mg_bLi_c)Si_4O_{10}F_2$ (in a formula, $0 < a \leq 1$, $2 \leq b < 3$, $0 \leq c < 1$, $a+b+2c=6$, and M express an ionic exchange nature cation, and are specifically sodium, lithium, etc.)

[0019]The montmorillonite used for this invention is expressed with a following formula, and is obtained by refining using elutriation processing etc. what is produced naturally.

$M_aSi(aluminum_{2-a}Mg)O_{10}(OH)_2$ and nH_2O (in a formula, M expresses cations, such as sodium, and is $0.25 \leq a \leq 0.6$.) n is zero or a positive integer.

Existence of the same type ionic substitution objects, such as magnesian montmorillonite and iron montmorillonite and iron magnesian montmorillonite, is known by montmorillonite, and these can also be used.

[0020]The loadings of the above-mentioned stratified mineral are 0.1 to 20 mass part preferably 0.01 to 100 mass part to monomer 100 mass part which forms polyamide or it. In less than 0.01 mass parts, since the fall of toughness becomes large in not acquiring the improvement effects made into the purpose of this invention, such as a mechanical strength and heat resistance, but exceeding 100 mass parts, it is not desirable.

[0021]It ejects carrying out melt kneading of lactam, a catalyst, an initiator, and the stratified mineral using a common ejection reaction extrusion machine as the polyamide resin composition of this invention, and a manufacturing method of the Plastic solid, and the method of polymerizing within a metallic mold is mentioned.

[0022]The most desirable method of manufacturing the polyamide resin composition of this invention is the method of obtaining by polymerizing a monomer to the monomer which forms polyamide, where specified quantity existence of the stratified mineral is recognized. In this case, a stratified mineral distributes finely enough in polyamide, and the effect of this invention shows up most notably. Making an issue of badness of the melting resin streak at the time of post processing which was a problem conventionally because it can fabricate to processed goods as it is at the time of a polymerization was lost.

[0023]To the polyamide resin composition of this invention, unless the characteristic and polymerization nature are spoiled greatly, it is also possible to add paints, a thermostabilizer, an antioxidant, a weathering agent, fire retardant, a plasticizer, a release agent, other reinforcement, etc. As a thermostabilizer or an antioxidant, hindered phenols, phosphorus compounds, hindered amine, sulfur compounds, a copper compound, the halogenides of an alkaline metal, or these mixtures can be used, for example. Additive agents, such as these thermostabilizers, an

antioxidant, and a weathering agent, are added at the time of melt kneading. As reinforcement, for example Clay, talc, calcium carbonate, zinc carbonate, Straw SUTONAITO, silica, alumina, magnesium oxide, a calcium silicate, Asbestos, sodium aluminate, calcium aluminate, sodium aluminosilicate, A magnesium silicate, glass balloons, carbon black, a zinc oxide, antimonous oxide, zeolite, a hide ROTARU side, a metal fiber, a metal whisker, ceramic whiskers, potassium titanate, boron nitride, graphite, glass fiber, carbon fiber, etc. are mentioned.

[0024]The resin composition of this invention can also build the target mold goods with the usual forming method in addition to the reaction injection molding which performs even metallic mold shaping at the time of a polymerization. For example, it is also possible thermofusion molding methods, such as injection molding, extrusion molding, entrainment shaping, and sinter molding, and to consider it as a thin film by the casting method from an organic solvent solution. The resin composition of this invention is notably improved compared with the case where a mechanical strength, heat resistance, and dimensional stability are polyamide independent, and there is little change of the mechanical properties by water absorption or a size. Mechanism elements and housing, such as a switch and a connector, [in / by the outstanding performance / in the resin composition of this invention / the electrical-and-electric-equipment field] It is used for a gear, a bearing retainer, etc. in optics, such as a under bonnet section article, exterior parts, an outer plate part article, or a reflector, or the machinery field in the automobile field.

[0025]When using the polyamide resin Plastic solid of this invention at a not less than 150 °C elevated temperature, the molecular weight fall by a catalyst residue may be caused. For this reason, it is possible to make a molecular weight fall hard to deactivate a catalyst by making it pass through underwater [not less than 80 °C], or carrying out steaming treatment, and to cause. Since time is taken too much below 80 °C, it is not desirable. Although it depends for processing time on the thickness of a Plastic solid, with 80-100 °C water, about 0.1 to 30 minutes is usually preferred in not less than 100 °C steaming treatment for 1 to 60 minutes.

[0026]

[Example]An example explains this invention still more concretely below. The raw material and measuring method which were used for evaluation of an example and a comparative example are as follows.

1. Raw material fluoride [(1)] mica CO-OP CHEMICAL CO., LTD. make swelling fluoride mica ME-100 was used.

(2) Na montmorillonite by montmorillonite Kunimine Industries KUNIPIA F was used.

(3) Talc (made by a Japanese talc company)

(4) Kaolin (made by a Shiraishi industrial company)

2. Measuring method (1) terminal-group-concentration amino group concentration titrated and asked for 1 g of polyamide 6 in the p-toluenesulfonic-acid solution of 0.1 N, after making it dissolve in 40 ml of m-cresol at 60 °C and cooling to a room temperature.

(2) It measured based on tensile strength and breaking extension degree ASTM D638.

(3) Based on Izod impact test ASTM D256, it carried out using the specimen of 3.2-mm thickness.

(4) Heat deflection temperature (DTUL)

It carried out based on ASTM D648. Load was performed by 1.82MPa.

(5) It measured based on rate ASTM Dof bending flexibility790.

(6) The specimen of the cylindrical shape (a coefficient of skid friction and the rough deposit abrasion loss outer diameter of 25.6 mm, 20 mm in inside diameter, and 15 mm in thickness) was produced by reaction injection molding. Subsequently, a Suzuki style frictional wearing characteristic testing machine is used, and it is planar pressure to a metal surface (S-45c) about this specimen. It rotated on condition of for 7.5-kg/cm² and revolving speed/of 18 m, and the coefficient of friction was calculated. Rough deposit abrasion loss was calculated by measuring the weight loss of the specimen after a 1000 wear test.

[0027]Heat melting of the moisture-regain% of epsilon caprolactam [8.0 kg of] of 0.03 mol was carried out at 100 °C as one-fold example affinity lactam, 300g of 0.3-mol % and swelling fluoride mica was added to this, and N-acetylcaprolactam was well agitated to it. This was slushed into the forming mold for specimens beforehand preheated to 150 °C, after adding after that ethylmagnesium star's picture 0.5 mol % and mixing quickly. Then, it was made to polymerize within the furnace adjusted at 160 °C. The polyamide resin Plastic solid was picked out from the metallic mold, and was made to fully cool in 20 minutes. Various kinds of quality assessments were performed using the obtained specimen.

[0028]The same operation as Example 1 was performed [all of 83g and except for having used

600g] for Example 2 - 3 swelling fluoride mica, the specimen was fabricated and various kinds of quality assessments were performed.

[0029]Except [all] having used Na montmorillonite as an example 4 stratified mineral, the same operation as Example 1 was performed, the specimen was fabricated and various kinds of quality assessments were performed.

[0030]Moisture-regain% of the epsilon caprolactam of 0.001 mol is used as 5-8-fold example affinity lactam, Except [all] having used 0.2, 0.13, 0. 1 or 0.07-mol % (respectively Examples 5, 6, 7, and 8), and ethylmagnesium star's picture 0.3 mol % for N-acetylcaprolactam, the same operation as Example 1 was performed, the specimen was fabricated and various kinds of quality assessments were performed.

[0031]Except having used omega-RAURO lactam of 0.01% of moisture regain as a nine-fold example affinity monomer, the same operation as Example 1 was performed, the specimen was fabricated and various kinds of quality assessments were performed.

[0032]The result of Examples 1-9 is shown in Table 1.

[0033]

[Table 1]

項目	実施例1	実施例2	実施例3	実施例4	実施例5	実施例6	実施例7	実施例8	実施例9
ポリアミド種類 層状鉱物種類 配合量(質量%)	ナイロン6 フッ素雲母 3. 6	ナイロン6 フッ素雲母 1. 0	ナイロン6 フッ素雲母 7. 0	ナイロン6 モンモリロナイト 3. 6	ナイロン6 フッ素雲母 3. 6	ナイロン6 フッ素雲母 3. 6	ナイロン6 フッ素雲母 3. 6	ナイロン6 フッ素雲母 3. 6	ナイロン12 フッ素雲母 3. 6
アミノ末端基量(モル/t)	2	1	2	1	2	1	1	1	1
相対粘度	4. 90	4. 93	4. 91	5. 01	7. 2	11. 4	15. 8	25. 9	4. 60
引張強度(MPa)	72	68	75	72	73	75	77	80	68
破断伸び(%)	35	68	18	35	30	31	30	33	37
アイゾット衝撃強度(J/m)	69	63	78	72	84	87	89	92	58
熱変形温度 1.82MPa (°C)	115	90	135	115	117	117	118	119	117
曲げ弾性率(GPa)	4. 0	3. 8	4. 2	4. 0	4. 2	4. 3	4. 3	4. 4	3. 9
耐摩耗性	摩耗量(mg/h)	1. 7	1. 9	1. 7	1. 7	1. 5	1. 4	1. 3	1. 5
	摩耗係数(-)	0. 25	0. 27	0. 25	0. 24	0. 23	0. 22	0. 20	0. 23

[0034]In comparative example 1 Example 1, except not having added swelling fluoride mica, same operation was performed, the specimen was fabricated and various kinds of quality assessments were performed.

[0035]Talc was used instead of the comparative example 2 - 4 swelling fluoride mica, and also the same operation as Examples 1-3 was performed, the specimen was fabricated and various kinds of quality assessments were performed.

[0036]Moisture-regain% of the epsilon caprolactam of 0.001 mol is used as 5 or 6-fold comparative example affinity lactam, Except having used 0. 2 or 0.1-mol % and ethylmagnesium star's picture 0.3 mol % for N-acetylcaprolactam, the same operation as the comparative example 2 was performed, the specimen was fabricated and various kinds of quality assessments were performed.

Kaolin was used instead of comparative example 7 swelling fluoride mica, and also the specimen was fabricated like Example 1, and various kinds of quality assessments were performed.

[0037]In comparative example 8 Example 9, swelling fluoride mica was added, twisted and cut, and also same operation was performed, the specimen was fabricated and various kinds of quality assessments were performed.

[0038]The result of the comparative examples 1-8 is shown in Table 2.

[0039]

[Table 2]

項目	比較例1	比較例2	比較例3	比較例4	比較例5	比較例6	比較例7	比較例8
ポリアミド種類 鉱物種類 配合量(質量%)	ナイロン6 なし	ナイロン6 タルク 3. 6	ナイロン6 タルク 1. 0	ナイロン6 タルク 7. 0	ナイロン6 タルク 3. 6	ナイロン6 タルク 3. 6	ナイロン6 カオリン 3. 6	ナイロン12 なし
アミノ末端基量(モル/t)	2	2	1	1	1	2	1	1
相対粘度	4. 89	4. 88	4. 87	4. 88	7. 5	15. 6	4. 90	4. 61
引張強度(MPa)	65	60	58	64	66	68	67	42
破断伸び (%)	160	3. 4	4. 5	2. 5	3. 5	3. 7	2. 9	230
アイゾット衝撃強度(J/m)	51	56	53	59	60	62	57	46
熱変形温度 1.82MPa (°C)	55	63	60	72	67	69	65	53
曲げ弾性率(GPa)	3. 2	3. 5	3. 3	3. 6	3. 7	3. 8	3. 5	3. 0
耐摩耗性	摩耗量(mg/h)	2. 5	2. 3	2. 5	2. 2	2. 0	1. 9	2. 4
	摩耗係数(-)	0. 35	0. 34	0. 34	0. 33	0. 30	0. 28	0. 31

[0040]

[Effect of the Invention]According to this invention, a mechanical strength and heat resistance are notably improved compared with a polyamide independent, and there are few falls of

toughness and the outstanding impact strength and the polyamide resin composition which has abrasion resistance can be obtained.

[Translation done.]

